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(54) Title: WHITE POLYLACTIC ACID FILM

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Specification

(57) [Abstract]

[Purpose] The purpose of the present invention is to produce a white film having low-density and good cushioning properties, with an absence of problems at the time of disposal.

[Means of solution] The white polylactic acid film of the present invention includes polylactic acid and a resin incompatible with the polylactic acid as the main constitutive components; also, the film has fine voids inside.

[Claims of the invention]

[Claim 1] A white polylactic acid film characterized by the fact that the polylactic acid and a resin incompatible with the polylactic acid are included as the main constitutive components, with the film having fine voids inside.

[Claim 2] The white polylactic acid film described in Claim 1, characterized by the fact that the aforementioned incompatible resin is a thermoplastic resin.

[Claim 3] The white polylactic acid film described in Claim 2, characterized by the fact that the aforementioned thermoplastic resin is a polyester consisting of an acid component and a glycol component.

[Claim 4] The white polylactic acid film described in Claim 3, characterized by the fact that the aforementioned polyester is one in which the main acid component is terephthalic acid and the main glycol component is ethylene glycol.

[Claim 5] The white polylactic acid film described in Claim 2, characterized by the fact that the aforementioned thermoplastic resin is a polyolefin.

[Claim 6] The white polylactic acid film described in Claim 5, characterized by the fact that the aforementioned polyolefin is a polypropylene.

[Claim 7] The white polylactic acid film described in one of Claims 1 to 6, characterized by the fact that the aforementioned white polylactic acid film has an apparent density in the range of 0.30 to 1.24 g/cm³.

[Detailed description of the invention]

[0001]

[Technical field of the invention] The present invention pertains to a white polylactic acid film; it further pertains to a white polylactic acid film with superior whiteness and cushioning properties and that has voids inside, retaining the features of the polylactic acid, and does not accumulate under natural conditions after disposal.

[0002] In the past, for producing a white film having fine voids inside, a film production method consisting of mixing a polyethylene terephthalate resin with a resin incompatible with said resin and forming a film, then drawing biaxially to form fine voids with the incompatible resin acting as nuclei, has been known. In this case, a polyolefin resin is used as the aforementioned incompatible resin, in many cases, and polypropylene, polymethylpentene, polystyrene, etc., are known. Furthermore, the aforementioned white film is used for image receptor films, labels, etc.

[0003] However, the above-mentioned white films used in the past do not undergo any decomposition at all in the natural environment, or the decomposition rate is very low; thus,

when thrown out and buried in the earth after use, the film remains semi-permanently on the ground or in the earth. Furthermore, when dumped in the sea, the scenery and habitat of marine life are destroyed. Furthermore, when disposed of by way of incineration, an increase in consumption and waste treatment pose social problems as a result of the accelerated deterioration of incinerators caused by the high combustion heat.

[0004] Meanwhile, a white film made of a biodegradable polylactic acid has been proposed (Japanese Kokai Patent Application No. Hei 11[1999]-268404), but achieving a good balance between the whiteness and cushioning properties and low-density is difficult since an increase in voids is less likely to be achieved, based on the inorganic filler used. When the particle diameter of the inorganic filler is increased in an attempt to increase the size of the voids, the stretchability is reduced, and when the amount of inorganic filler added is increased in an effort to increase the number of voids, the density is increased and the method has many problems associated with its use.

[0005]

[Problems to be solved by the invention] The purpose of the present invention is to eliminate the problems in the prior art mentioned above and to produce a white film having a low-density and good cushioning properties, with an absence of problems at the time of disposal.

[0006]

[Means to solve the problems] In order to eliminate the aforementioned problems, the method described below is used in the present invention. Thus, the white polylactic acid film of the present invention includes polylactic acid and a resin incompatible with the polylactic acid as the main constitutive components, with the film having fine voids inside.

[0007]

[Method to solve the problems] As a result of much research conducted on this subject, that is, on white films with low density and having superior whiteness and cushioning properties, along with an absence of problems at the time of disposal in an effort to eliminate the above-mentioned existing problems, the inventors discovered that the aforementioned problems could be entirely eliminated when a specific resin is mixed with polylactic acid and forms a film having voids inside it.

[0008] The polylactic acid used in the present invention is either a polylactic acid, a copolymer of lactic acid and another hydroxycarboxylic acid, or a mixture thereof; in order to improve handling, processability, and physical properties, an appropriate amount of additives such as plasticizers, lubricants, heat stabilizers, anti-coloring agents, ultraviolet-light absorbers, light stabilizers, and antioxidants may be included, as needed.

[0009] For the lactic acid, L-lactic acid and D-lactic acid can be mentioned; for the other hydroxycarboxylic acid, glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-

hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid can be mentioned.

[0010] The incompatible resin with polylactic acid used in the present invention is a resin that exhibits phase separation after mixing and being formed into a sheet; it is preferably a thermoplastic resin, and ideally is a polyester or polyolefin composed of an acid component and a glycol component.

[0011] For polyesters composed of an acid component and a glycol component, a polyester having an aromatic dicarboxylic acid, aliphatic dicarboxylic acid, or alicyclic dicarboxylic acid and a glycol as the main constitutive components can be mentioned. For the aforementioned aromatic dicarboxylic acid component, for example, terephthalic acid, isophthalic acid, phthalic acid, 1,4-naphthalene dicarboxylic acid, 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid, 4,4'-diphenylether dicarboxylic acid, and 4,4'-diphenylsulfone dicarboxylic acid can be mentioned; among those listed above, terephthalic acid, isophthalic acid, and 2,6-naphthalene dicarboxylic acid are especially desirable. Furthermore, for the aliphatic dicarboxylic acid component, for example, adipic acid, suberic acid, sebacic acid, dodecanoic acid, etc., can be mentioned. Furthermore, for the alicyclic dicarboxylic acid component, for example, 1,4-cyclohexane dicarboxylic acid, etc., can be mentioned. One, two, or more different types of the above-mentioned acid components may be used; furthermore, an oxy acid such as hydroxybenzoic acid may be partially copolymerized as well. For the glycol component, for example, ethylene glycol, 1,2-propanediol, 1,3-propanediol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanenedimethanol, 1,4-cyclohexanenedimethanol, diethylene glycol, triethylene glycol, polyalkylene glycol, 2,2-bis(β -hydroxyethoxyphenyl) propane, etc., can be mentioned. Furthermore, one, two, or more different types of the above-mentioned glycol components may be used.

[0012] For specific examples of polyesters used in the present invention, polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polyhexamethylene terephthalate, a copolymer of ethylene terephthalate and ethylene isophthalate, a copolymer of ethylene terephthalate and ethylene naphthalate, etc., can be mentioned.

[0013] Furthermore, for the polypropylene resin, polypropylene, polyethylene, polymethylpentene, polystyrene, and mixtures or copolymers thereof can be mentioned.

[0014] In the present invention, the resin incompatible with polylactic acid is dispersed in the polylactic acid, with the mixing ratio being in the range of 1 wt% to 30 wt%, preferably 2 wt% to 25 wt%, and ideally 3 wt% to 20 wt%, from the standpoint of whiteness, low-density, productivity, and mechanical strength. The polylactic acid film mixed with the aforementioned incompatible resin forms fine voids having the incompatible resin as a nucleus upon performing biaxial drawing. Furthermore, an increase in properties such as whiteness, mechanical strength,

and reduced density is achieved when biaxial drawing is done.

[0015] The thickness of the film of the present invention is in the range of 5 to 1000 µm, preferably 8 to 500 µm, and ideally 10 to 300 µm. When the thickness is in the range of 5 µm to 1000 µm, a good handling property can be achieved.

[0016] In the present invention, it is desirable when a layer essentially with an absence of voids is laminated onto at least one surface, preferably both surfaces, of a film having a polylactic acid and a resin incompatible with the polylactic acid as main constitutive components, and that has fine voids inside so as to prevent detachment of the incompatible resin during the course of production of the film, and from the standpoint of surface smoothness and high adhesion. For the resin used for the layer essentially without voids, the above-mentioned polylactic acids, polyesters, and polyolefins can be mentioned. The thickness of the aforementioned laminated layer is not especially limited, with 1 to 30% of the total film thickness being desirable, and with 2 to 20% being more desirable.

[0017] Furthermore, in order to further increase the whiteness of the film of the present invention, a white pigment may be included in the film having voids and/or the layer without voids. For the white pigment used in this case, for example, titanium dioxide, barium sulfate, zinc oxide, calcium carbonate, etc., can be mentioned.

[0018] The method of manufacturing the white polylactic acid film of the present invention is explained further below.

[0019] For the polymerization method of polylactic acid, the polycondensation method, ring-opening polymerization method, etc., may be used; furthermore, in order to increase the molecular weight, a small amount of a chain extender, for example, a diisocyanate compound, diepoxy compound, acid anhydride, etc., may be used. For the weight-average molecular weight of the polymer produced as described above, a value in the range of 10,000 to 100,000 is desirable from the standpoint of practical properties and moldability.

[0020] In the present invention, the method used for mixing the incompatible resin with the polylactic acid produced above is not especially limited, and conventional mixing methods may be used. For example, a method in which dry incompatible resin chips are added to polylactic acid chips, with mixing being done by a ribbon blender, tumbler, Henschel mixer, etc., and with further kneading being done by a Banbury mixer or uniaxial or biaxial extruder at a temperature of 170 to 250°C to produce a composition in the form of pellets, rods, or powder, can be mentioned. Furthermore, a master batch in which the incompatible resin is mixed with the polylactic acid at a high concentration, then mixed with polylactic acid to produce a composition with the final concentration, may be produced by the above-mentioned method.

[0021] The method used for the production of a film from the composition produced as described above is not especially limited. For example, the aforementioned composition is vacuum dried at

100 to 140°C and supplied to an extruder, then hot-melt mixing is done at a temperature above the melting point. For the extrusion temperature, a temperature of 200 to 270°C is desirable. Furthermore, the molten polymer is extruded from a T-die having a discharge slit, then chilled and solidified on a chill roll to produce a cast film. In order to increase adhesion between the molten sheet and chill roll, use of electrostatic adhesion or the surface coating method is desirable. When the layer with an absence of voids is provided, coextrusion can be used effectively.

[0022] Furthermore, biaxial drawing of the aforementioned cast film is done. For the biaxial drawing method used in this case, a method in which vertical drawing is done by roll drawing, then with horizontal drawing by a tenter; a sequential biaxial drawing method where the above-mentioned order is reversed; or simultaneous biaxial drawing using a tenter may be used.

[0023] As the temperature used for biaxial drawing, a temperature near the glass transition temperature of the polymer, for example, 60 to 120°C, is desirable. For the drawing ratio, 2.5 to 10 times in each direction is desirable. Furthermore, additional drawing can be done after biaxial drawing.

[0024] Heat-treatment is provided for the film produced as described above. For the heat-treatment temperature used in this case, a temperature of 90 to 160°C is desirable, with 110 to 140°C being especially desirable. The heat-treatment time used is preferably in the range of 1 second to 5 minutes. An adjustment of the thermal shrinkage property is possible based on the above-mentioned heat-treatment conditions. For example, after the heat-treatment, rapid cooling and slow cooling can be provided for the film; furthermore, an intermediate cooling zone may be provided and adjustment of the thermal shrinkage stress can be achieved. Relaxation in the vertical direction or horizontal direction may be provided during the course of the heat-treatment or in the slow cooling zone that follows.

[0025] In the film of the present invention, a coating layer may be provided for improvement of the wettability or adhesion to one or both surfaces. From the standpoint of explosion resistance and environmental pollution, a dispersion, emulsion, or suspension is used for the coating solution. The coating layer may be provided for the biaxially drawn film after crystal orientation or before the completion of crystal orientation; the latter method is especially desirable to further enhance the effect of the present invention.

[0026] The coating method used in this case is not especially limited, and coating can be done by a roll coater, gravure coater, reverse coater, kiss coater, bar coater, etc. Furthermore, a corona treatment may be applied to the coating surface in air or another atmosphere, as needed, before coating.

[0027] Furthermore, the coating layer of the present invention may include defoaming agents, ultraviolet-light absorbers, dyes, etc.

[Methods for measurement of properties]

(1) Film formation

An evaluation was made for problems such as rupturing of the film and contamination of the film-forming machine, etc., at the time of film formation.

[0028] O: stable film formation, very good.

[0029] Δ: occasional film rupturing was observed or contamination of drums and rolls in the film-forming machine was observed; film-forming property is inferior.

[0030] X: Frequent rupturing of film; film-forming property is poor.

[0031] In this case, those with O and Δ can be used in practice.

(2) Specific gravity

A sample is cut with dimensions of 50 mm (TD) × 60 mm (MD), and measurements are made by the high precision electro-aerometer SD-120L (product of Miraju Trading [transliteration] Co., (Ltd.)) using the water displacement method, then the specific gravity is calculated.

(3) Degree of whiteness (%)

The spectro-color difference meter, SE-2000 (product of Nippon Denshoku Co., (Ltd.)) is used; three excitation values, X, Y, and Z are measured, and the calculation is made according to the formula shown below.

[0032]

$$\text{Degree of whiteness (\%)} = 4 \times 0.847 \times Z - 3 \times Y$$

(4) Cushioning property (%)

A standard probe (No. 90030) is attached to a dial gauge (product of Sanpo Manufacturer, No. 2109-10), a 50-g and 500-g load are each applied to the top of the probe, and the thickness of the film is measured; the calculation is done according to the formula shown below.

[0033] Cushioning property (%) =

$$\{1 - (\text{thickness under 500 g load}) / (\text{thickness under 50 g load})\} \times 100$$

For a good cushioning property, a value of at least 5% is desirable.

[0034]

[Application Examples] In the following, the present invention is explained in further detail with application examples, but the present invention is not limited to those examples.

[0035] Application Example 1

Dry blending was performed for 100 parts by weight of poly(L-lactic acid) (mixing ratio with D modification of 1.2%, glass transition temperature 64°C) pellets with a molecular weight of 100,000 and 1.5 parts by weight of ethylene terephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio) pellets, then the mixture was supplied to a biaxial extruder having different rotational directions, with extrusion and pelletization being done at 220°C.

[0036] The pellets produced were vacuum dried for 5 hours at 120°C, then supplied to an extruder; melting was done at 235°C and hot-melt extrusion was done from the T-die at the end of the extruder onto a rotating chilled drum to form a sheet by the electrostatic adhesion method. When the extrusion was chilled and solidified, an amorphous sheet was produced.

[0037] Subsequently, sequential biaxial drawing was done for the aforementioned amorphous sheet using heated rolls to 3.0 times in the longitudinal direction at 68°C, then to 3.2 times in the width direction at 68°C. A heat-treatment was then applied at 140°C to produce a biaxially drawn film with a thickness of 50 µm. An excellent film stability was achieved.

[0038] Properties of the resulting film are shown in Table I; low density, a superior degree of whiteness, and a superior cushioning property were achieved.

[0039] Comparative Example 1

For 100 parts by weight of the poly(L-lactic acid) used in Application Example 1, 15 parts by weight of titanium dioxide having a mean particle diameter of 0.3 µm were added and mixing was done; the mixture was then supplied to a biaxial extruder with different rotating directions, with extrusion and pelletization being done at 220°C.

[0040] For the pellets produced, vacuum drying was done for 5 hours at 120°C; they were then supplied to an extruder. Melting was done at 235°C and hot-melt extrusion was done from the T-die at the end of the extruder onto a rotating chilled drum to form a sheet by the electrostatic adhesion method; the extrusion was chilled and solidified to produce an amorphous sheet.

[0041] Subsequently, sequential biaxial drawing was done for the aforementioned amorphous sheet using heated rolls to 3.0 times in the longitudinal direction at 68°C, then to 3.2 times in the width direction at 68°C, but frequent film rupturing made it impossible to form a film.

[0042] Properties of the portion of the film salvaged are shown in Table I; as shown, a reduction in density was not possible.

[0043] Comparative Example 2

In Comparative Example 1, the mixing ratio of the titanium oxide was changed to 5 parts by weight and film formation was done as described above. Film formability was indicated by a Δ.

[0044] Furthermore, properties of the film obtained are shown in Table I; the degree of whiteness and cushioning property were poor.

[0045] Comparative Example 3

In Comparative Example 2, the titanium dioxide with a mean particle diameter of 0.3 µm was changed to calcium carbonate with a mean particle diameter of 1.5 µm; film formation was done as described above, but frequent film rupturing made it impossible to form a film.

[0046] Properties of the portion of the film salvaged are shown in Table I; as shown, the degree of whiteness and cushioning property are poor.

[0047] Application Examples 2 to 5

In Application Example 1, the type and mixing ratio of the pellets mixed with poly(L-lactic acid) pellets were changed as shown in Table I below, with biaxial films being produced in the same manner.

[0048] Properties of films produced and evaluation results of the film quality are shown in Table I; excellent results were achieved with the films of the present invention.

[0049] Application Example 6

Dry blending was done for 100 parts by weight of poly(L-lactic acid) (mixing ratio with D modification of 3%, glass transition temperature 63°C) pellets with a molecular weight of 100,000, 10 parts by weight of ethylene terephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio) pellets, then supplied to a biaxial extruder having different rotating directions, with extrusion and pelletization being done at 220°C.

[0050] For the pellets produced, vacuum drying was done for 5 hours at 120°C, then supplied to an extruder. Melting was done at 235°C and hot-melt extrusion was done from a T-die at the end of the extruder onto a rotating chill drum to form a sheet by electrostatic adhesion; the extrusion was chilled and solidified to produce an amorphous sheet.

[0051] Subsequently, sequential biaxial drawing was done for the aforementioned amorphous sheet using heated rolls to 4.0 times in the longitudinal direction at 70°C, then to 4.0 times in the width direction at 68°C. A heat-treatment was then applied at 140°C to produce a biaxially drawn film with a thickness of 50 µm. Excellent film stability was achieved.

[0052] Properties of the films produced are shown in Table I; low density, superior degree of whiteness, and superior cushioning properties were achieved.

[0053] Application Example 7

A coextruder-laminator capable of forming a double lamination film consisting of a main extruder and a sub-extruder in which a sub-layer is formed on both sides of the main layer was used. Pellets produced by extruding a dry blend of poly(L-lactic acid) pellets and ethylene terephthalate-ethylene isophthalate copolymer pellets used in Application Example 1 were supplied to the main extruder, with pellets produced by extruding a mixture of poly(L-lactic acid) pellets and titanium dioxide used in Comparative Example 2 being supplied to the sub-extruder. In this case, the pellets supplied to each extruder were vacuum dried for 5 hours at 120°C ahead of time. Both extruders were heated to 235°C; hot-melt extrusion was done from T-dies at the end of the extruders onto a rotating chill drum to form a sheet by the electrostatic adhesion method, then the extrusion was chilled and solidified to produce an amorphous sheet having a sub-layer/main layer/sub-layer thickness ratio of 5/90/5.

[0054] Subsequently, sequential biaxial drawing was done for the aforementioned amorphous sheet using heated rolls to 3.0 times in the longitudinal direction at 68°C, then to 3.2 times in the width direction at 68°C. A heat-treatment was then applied at 140°C to produce a biaxially

drawn film with a thickness of 50 μm . Excellent film stability was achieved.

[0055] Properties of the film produced are shown in Table I below; low density, superior degree of whiteness, and a superior cushioning property were achieved.

[0056]
[Table I]

Table I

	Layer structure	Main polymer	Composition	Mixing ratio	Drawing method	Film formability	Specific gravity	Degree of whiteness	Cushioning properties
Application Example 1	Single layer	Poly(L-lactic acid)	Ethyleneterephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio)	15 parts by weight	Sequential biaxial drawing	○	0.63	115%	20%
Application Example 2	Single layer	Poly(L-lactic acid)	Ethyleneterephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio)	5 parts by weight	Sequential biaxial drawing	○	0.87	100%	12%
Application Example 3	Single layer	Poly(L-lactic acid)	Ethyleneterephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio)	30 parts by weight	Sequential biaxial drawing	△	0.40	120%	45%
Application Example 4	Single layer	Poly(L-lactic acid)	Polyethylene terephthalate	10 parts by weight	Sequential biaxial drawing	○	0.71	107%	22%
Application Example 5	Single layer	Poly(L-lactic acid)	Polypropylene	10 parts by weight	Sequential biaxial drawing	○	0.60	112%	24%
Application Example 6	Single layer	Poly(L-lactic acid)	Ethyleneterephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio)	15 parts by weight	Sequential biaxial drawing	○	0.57	117%	27%
Application Example 7	Three-layer structure of sub-layer/main layer/sub-layer	Main layer	Ethyleneterephthalate-ethylene isophthalate copolymer (18 mol% isophthalic acid copolymerization ratio)	15 parts by weight	Main layer				
		Sub-layer	Poly(L-lactic acid)		Sub-layer				
			Titanium dioxide with mean particle diameter of 0.3 μm	5 parts by weight					
Comparative Example 1	Single layer	Poly(L-lactic acid)	Titanium dioxide with mean particle diameter of 0.3 μm	15 parts by weight	Sequential biaxial drawing	×	1.30	93%	5%
Comparative Example 2	Single layer	Poly(L-lactic acid)	Titanium dioxide with mean particle diameter of 0.3 μm	5 parts by weight	Sequential biaxial drawing	△	1.28	88%	4%
Comparative Example 3	Single layer	Poly(L-lactic acid)	Calcium carbonate with mean particle diameter of 1.5 μm	15 parts by weight	Sequential biaxial drawing	×	1.18	105%	7%

[0057] As is clearly shown in Table I, in comparison to films produced in Comparative Examples 1 to 3, excellent film formability was achieved, along with reduced density, high degree of whiteness, and superior cushioning properties among films produced in Application Examples 1 to 7.

[0058]

[Effect of the invention] According to the present invention, it is possible to produce a white film having a low-density and good cushioning property, with an absence of problems at the time of disposal.

**JAPANESE PATENT APPLICATION NO. 2002-146071
WHITE POLYLACTIC ACID FILM**

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